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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: <b>PCT/US99/07482</b> (22) International Filing Date: <b>5 April 1999 (05.04.99)</b>  (30) Priority Data: 09/058,618      10 April 1998 (10.04.98)      US 09/277,454      26 March 1999 (26.03.99)      US  (71) Applicant: <b>FERRO CORPORATION [US/US]; 1000 Lakeside Avenue, Cleveland, OH 44114 (US).</b>  (72) Inventors: <b>PRENDERGAST, John, E.; 45 South Kashong Drive, Geneva, NY 14456 (US). HER, Yieshein; 3430 West Lake Road, Canandaigua, NY 14424 (US). BABU, Suryadevara, V.; 24 Haggerty Road, Potsdam, NY 13676 (US). LI, Yuzhuo; 55 Pine Street, Potsdam, NY 13676 (US). HARIHARAPUTHIRAN, Mariappan; Apartment 34, 43 Market Street, Potsdam, NY 13676 (US).</b>  (74) Agent: <b>CLARK, Kenneth, A.; Rankin, Hill, Porter &amp; Clark LLP, Suite 700, 925 Euclid Avenue, Cleveland, OH 44115-1405 (US).</b>		(81) Designated States: <b>CA, JP, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>  <b>Published</b> <i>With international search report.</i>
(54) Title: <b>SLURRY FOR CHEMICAL-MECHANICAL POLISHING METAL SURFACES</b>  (57) Abstract <p>The present invention provides a slurry for chemical-mechanical polishing metal surfaces which significantly increases the removal rate and is capable of polishing metals which are inert to most common oxidizing agents. The slurry is particularly useful for polishing metal layers on semiconductor wafer substrates. The slurry includes water, abrasive particles, and an oxidizing solution. In one preferred embodiment, the oxidizing solution comprises one or more water soluble peroxides, one or more amino acids, and one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred. In another preferred embodiment, the oxidizing solution comprises one or more water soluble peroxides, one or more organic amines, and optionally one or more metals and/or compounds containing metals.</p>		

**Title: SLURRY FOR CHEMICAL-MECHANICAL  
POLISHING METAL SURFACES**

**Background Of The Invention**

**Field of the Invention**

The present invention concerns chemical compositions for use in polishing. The present invention relates to a polishing slurry for the chemical-mechanical polishing of metal surfaces.

**Description of the Related Art**

Chemical-mechanical polishing ("CMP") is a technology which has its roots in the pre-industrial era. In recent years, CMP has become the technology of choice among semiconductor chip fabricators to polish or planarize the surface of semiconductor chips after each metal containing circuit pattern layer is laid down. CMP technology is well-known, and is typically accomplished by applying pressure with a polishing pad saturated with a metal polishing slurry to the surface to be polished.

Examples of prior art patents that concern CMP include U.S. Patent No. 4,959,113 issued to Roberts that discloses a slurry for CMP metal surfaces which generally comprises: (i) water; (ii) abrasive particles; and (iii) a salt. U.S. Patent No. 5,354,490 issued to Yu et al. discloses a slurry for the CMP of predominantly copper metal surfaces which generally comprises: (i) water; (ii) abrasive particles; and (iii) a component selected from the group consisting of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{AgNO}_3$ . U.S. Patent No. 5,527,423 issued to Neville et al. discloses a slurry for CMP metal surfaces which generally comprises: (i) water; and (ii) high

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and amino acid results in the accelerated generation of hydroxyl radicals and yields a much more effective polishing composition.

In another preferred embodiment, the oxidizing solution (iii) comprises: (a') water soluble peroxide; and (b') organic amine. The use of organic amine in combination with water soluble peroxide also results in the accelerated generation of hydroxyl radicals. To further increase the generation of hydroxyl radicals, such oxidizing solution can further optionally comprise one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred.

These and other aspects and advantages of the present invention will be readily understood and appreciated by those skilled in the art from the following detailed description of the invention with the best mode contemplated for practicing the invention in view of the accompanying drawings.

#### **Brief Description Of The Drawings**

In the annexed drawings:

FIG. 1 is a graph illustrating that in a slurry of the present invention the rapid formation of hydroxyl radicals occurs when hydrogen peroxide, glycine and copper nitrate are present at the same time;

FIG. 2 is a graph illustrating that in a slurry of the present invention the rate of hydroxyl radical formation varies when other amino acids are substituted for glycine:

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The abrasive particles (ii) used in the slurry may comprise any one or a mixture of a variety of abrasive particles that are conventionally utilized in CMP slurries. Examples of suitable abrasive particles include alumina, silica, silicon nitride, silicon carbide, ceria, copper oxide, iron oxide, nickel oxide, manganese oxide, tin oxide, titania, titanium carbide, tungsten oxide, yttria and zirconia, or a combination thereof. The abrasive particles preferably have a mean size ranging from about 0.02 to about 1.0 micrometers, with a maximum size of less than about 10 micrometers. The abrasive particles are preferably present in the slurry in an amount of from about 0.1 to about 60% by weight of the slurry.

The oxidizing solution (iii) used in the slurry must rapidly generate more hydroxyl radicals than would otherwise be generated by hydrogen peroxide alone. The applicants have found that the presence of a relatively large concentration of hydroxyl radicals greatly enhances the polishing rate of metals, including metals such as tantalum which are inert to most oxidizing agents. In one preferred embodiment, the oxidizing solution (iii) comprises: (a) one or more water soluble peroxides; (b) an amino acid or mixture of amino acids; and (c) one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred. In another preferred embodiment, the oxidizing solution (iii) comprises: (a') one or more water soluble peroxides; (b') one or more organic amines; and optionally (c') one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred.

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copper salicylate, copper selenate, copper sulfate, and copper tartrate, or a combination of the foregoing. Similar forms of chromium, cobalt, iron, lead, nickel, palladium, rhodium, samarium, and scandium would also be suitable for use in the invention. The metals and/or compounds containing metals are preferably present in the slurry in an amount of from about 0.1% to about 10% by weight.

The organic amine (iii)(b') used in the slurry may comprise primary amine ( $RNH_2$ ), secondary amine ( $R_2NH$ ), tertiary amine ( $R_3N$ ), mixtures thereof, and/or an amine containing all or some of these three types of amine moieties, where R is an aliphatic hydrocarbon or an aromatic hydrocarbon. In the currently preferred embodiment, the organic amine is bis(hexamethylene)triamine ( $H_2N(CH_2)_6NH(CH_2)_6NH_2$ ). The organic amine is preferably present in the slurry in an amount of from about 0.1% to about 10% by weight.

The slurry according to the present invention effectively polishes metals throughout a wide pH range. For semiconductor polishing applications, it is generally preferred to polish the metal layers deposited on the substrate rapidly without etching or polishing the substrate material at all. It has been found that polishing with a slurry having a pH greater than about 7 will sometimes cause the substrate material to become polished or etched. However, when the pH of the slurry is adjusted such that it is more acidic, the substrate material will not become polished or etched. Accordingly, for such applications the slurry is optionally adjusted to a pH of from about 2 to about 5 by adding common acids such as hydrochloric acid, nitric acid, sulfuric acid, acetic acid, phosphoric acid or other conventional acids.

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The metal surface is then polished with the composition using a felt or other polishing pad. Typical pads include Rodel Suba 500 pads, IC 1000 pads or similar commercially available pads. Although polishing is usually conducted at room temperature, it will be appreciated that an increase in the temperature generally results in an increase in the concentration of hydroxyl radicals formed.

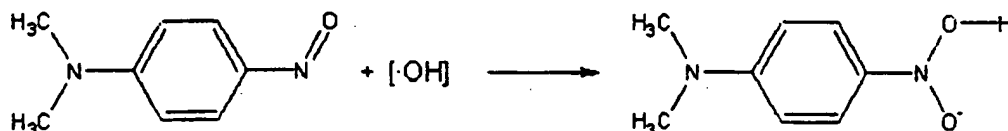
In addition to providing a slurry, the polishing composition of the present invention may be generated in situ. More particularly, for example, the metals and/or compounds containing metals (iii)(c) and the amino acids (iii)(b) could be added on the metal surface to be polished to a solution of water (i), abrasive particles (ii), and water soluble peroxide (iii)(a). Alternatively, for example, a solution of the metals and/or compounds containing metals (iii)(c), amino acids (iii)(b), and water soluble peroxide (iii)(a) could be added on the polishing surface to a solution of water (i) and abrasive particles (ii). It will be appreciated that since the order of addition is not per se critical, any number of a multitude of possible combinations for forming the slurry in situ could be employed. However, because peroxides decompose rapidly once being mixed with the other components, it is preferable to keep peroxides from the other components in the slurry formulation until immediately prior to use.

In another aspect of the present invention the polishing slurry of the present invention may be formed by incorporating a portion of the components of the slurry in a polishing pad. For example, the amino acids (iii)(b), abrasive particles (ii) and the metals and/or compounds containing metals (iii)(c) could be incorporated directly in the polishing pad, and a solution of water (i) and water soluble peroxide (iii)(a) could then be added at the polishing surface

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Preface to Examples

As noted by Liu, X., DiLabi, G.A., Martin, F., and Li, Y in "Catalytic Formation of Hydroxyl Radical from Hydrogen Peroxide in the Presence of an Amine", submitted to J.A.O.S. in 1998, the formation of hydroxyl radicals can be quantitatively analyzed using a hydroxyl radical trap such as N,N-dimethyl-4-nitrosoaniline (PNDA). As the hydroxyl radical is formed, it adds to the PNDA via the reaction described below:



PNDA has a unique and strong absorption in the visible region at 440 nm whereas the product of the reaction between PNDA and a hydroxyl radical has a weak absorption at 440nm. Thus, the amount of hydroxyl radical formed is detected by the disappearance of PNDA over time as indicated by subsequent decreasing absorptions at 440nm.

The concentration of hydroxyl radical can be calculated by the rate equation:

$$-\frac{d[\text{PNDA}]}{dt} = k'[\text{PNDA}][\cdot\text{OH}]$$

When assuming  $[\cdot\text{OH}]$  is in steady state, the above-equation becomes:

$$-\frac{d[\text{PNDA}]}{dt} = k[\text{PNDA}]$$



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The various combinations of components discussed below were tested for their effectiveness in promoting the formation of hydroxyl radical over a thirty minute period. The hydroxyl radical concentration was then calculated for each combination. All percents are by weight unless otherwise stated.

5           In a small vial, 9.0 +/- 0.1 ml doubly distilled H<sub>2</sub>O was added to 0.6 +/- 0.02 ml 30% H<sub>2</sub>O<sub>2</sub>. The solution's pH was regulated to 8.45 +/- 0.05 using small drops of 1N NaOH and 1N H<sub>2</sub>SO<sub>4</sub>. In a separate container, 0.08 +/- 0.01 ml of 5mM PNDA was added to the solution followed immediately by addition of 0.36 +/- 0.02ml of a 5mM metal ion solution of the metals shown in Table 1 below and 0.1% glycine. Each reaction solution's intensity at  
10           440nm was measured for 30 minutes in 5 minute intervals at 25°C. Table 1 below sets forth the steady-state hydroxyl radical concentration for each trial as determined using the kinetics equation discussed above.

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Example 2

The solutions shown in Table 2 below were prepared according to the procedures set forth in Example 1. Each solution's intensity at 440nm was measured for 30 minutes in 5 minute intervals at 25°C. Table 2 below sets forth the hydroxyl radical concentration for each trial as determined using the kinetics equation discussed above.

Table 2

<u>Components of Trial</u>	<u>Slope of <math>\ln(A_0/A)</math></u>	<u><math>[\cdot\text{OH}]</math> (M)</u>
Cu + 0.1% glycine	0.03590	$2.87 \times 10^{-12}$
0.1% bis(hexamethylene)triamine	0.00264	$2.11 \times 10^{-13}$
Cu + 0.1% bis(hexamethylene)triamine	0.00552	$4.42 \times 10^{-13}$
0.5% bis(hexamethylene)triamine	0.01057	$8.46 \times 10^{-13}$
1.0% bis(hexamethylene)triamine	0.01436	$1.15 \times 10^{-12}$
Fe + 1.0% bis(hexamethylene)triamine	0.01456	$1.16 \times 10^{-12}$
Cr + 1.0% bis(hexamethylene)triamine	0.01385	$1.11 \times 10^{-12}$

Example 2 demonstrates that as the concentration of bis(hexamethylene)triamine approaches 1.0% by weight, it becomes a comparable hydroxyl radical promoter to a 0.1% glycine/Cu<sup>2+</sup> system. Example 2 also demonstrates that the addition of metal ions to a triamine solution sometimes increases the effectiveness of the triamine as a hydroxyl radical promoter.

Example 3

This example demonstrates that each of the components of the invention (i.e., for example, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), glycine (NH<sub>2</sub>CH<sub>2</sub>COOH), and copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>)) have to be present at the same time in order to generate large amounts of hydroxyl radicals (OH·).

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Example 5

This example demonstrates that copper nitrate can be replaced by other copper compounds, such as copper oxide (CuO) and elemental copper (Cu), for the purpose of forming hydroxyl radicals.

5           The same experiment as in Example 3 was again repeated, except that the copper nitrate is replaced by copper oxide powder or elemental copper powder. The concentration of hydrogen peroxide and glycine were 2% by weight and 1% by weight, respectively. The concentration of copper oxide and copper powders varied from 3 mg/10 ml to 10 mg/10 ml. The experiment results, as shown in Fig. 3, demonstrate that fast generation of hydroxyl radicals, as indicated by rapid reduction in PNDA concentration ( $A/A_0$ ), occurs when  
10           hydrogen peroxide, glycine, and copper oxide or element copper are present at the same time.

Example 6

This example shows that removal rate of tantalum (Ta) is significantly increased when polishing with the disclosed slurry formulation.

15           A tantalum disc is polished using a Struers polisher and Suba 500 pad. at a pressure of 6.3 psi, and a rotation speed of 90 rpm. Two CMP slurries were used as follows:

Slurry A contains: (1) 3% by weight alumina abrasive particles with a mean diameter of 0.35 micrometers and maximum diameter of 2.0 micrometers; and  
(2) 5% by weight hydrogen peroxide.

20           Slurry B contains: (1) 3% by weight alumina abrasive particles with a mean diameter of 0.35 micrometers and maximum diameter of 2.0 micrometers; (2)

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made without departing from the spirit or scope of the general inventive concept as defined  
by the appended claims and their equivalents.

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8. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said oxidizing solution further comprises one or more amino acids and one or more metals or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium.

5 9. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said amino acids are one or more selected from the group consisting of arginine, cysteine, glutamine, glutamic acid, glycine, histidine, phenylalanine, serine, and mixtures thereof.

10 10. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said amino acids are one or more selected from the group consisting of amino carboxylic acid, amino alkyl carboxylic acid, amino phenyl carboxylic acids, the sodium, potassium, and ammonium salts thereof, and mixtures thereof.

15 11. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said amino acids are present in said slurry in an amount of from about 0.1% to about 10% by weight.

20 12. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said metals and/or compounds containing metals are one or more selected from the group consisting of metal-acetate, metal-bromide, metal-butyrate, metal-chlorate, metal-chloride, metal-citrate, metal-fluoride, metal-formate, metal-gluconate, metal-glycinate, metal-hexafluorosilicate, metal-nitrate, metal-oxide powder, metal-hydroxide powder, elemental

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of these three types of amine moieties, and mixtures thereof, where R is an aliphatic hydrocarbon or an aromatic hydrocarbon.

17. The slurry for chemical-mechanical polishing metal surfaces as in claim 15 wherein said organic amine is present in said slurry in an amount of from about 0.1% to about 10% by weight.

18. The slurry for chemical-mechanical polishing metal surfaces as in claim 15 wherein said oxidizing solution further comprises one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium.

19. The slurry for chemical-mechanical polishing metal surfaces as in claim 15 wherein said abrasive particles comprise alumina having a mean diameter of about  $0.35\mu\text{m}$  and a maximum diameter of less than about  $2.0\mu\text{m}$ , said abrasive particles being present in said slurry in the amount of about 3% by weight, said water soluble peroxide comprises hydrogen peroxide, said water soluble peroxide being present in said slurry in the amount of up to about 30% by weight, said oxidizing solution further comprises an organic amine, said organic amine comprising bis(hexamethylene)triamine and being present in said slurry in an amount of up to about 10% by weight.

20. A method of polishing a metal surface comprising the steps of:

- I. providing a metal surface to be polished;
- II. providing a polishing pad;

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/07482

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) :H01L 21/00; B44C 1/22; C09G 1/00 US CL :216/88, 89, 90; 438/692, 693 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 216/88, 89, 90; 438/692, 693 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS Search Terms: chemical mechanical polishing, cmp, metal		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,930,870 A (BASD) 6 January 1976, abstract	12-14
X	US 5,575,885 A (HIRABAYASHI et al) 19 November 1996, Figs. 1 and 2; abstract; col. 2, lines 28-32; col. 4, lines 60-68; col. 5, lines 9-25	1-11, 15-20
X, P	US 5,770,095 A (SASAKI et al) 23 June 1998, Fig. 1; abstract; col. 3, lines 32-35; col. 4, lines 1-10; col. 6, lines 1-12 and 37-45; col. 8, lines 5-20 and 48-49	1-11, 15-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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